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The Physical Chemistry of the Carbonizing Process

By ALAN A. CLAFLIN

The summary of this paper shows that researches in leather chemistry show protein fibres combine as a base with acid radicles, that the content of water and concentration of acid in the fibre changes with the concentration of the acid in the external water, and that with these changes the physical condition of the fibre changes.

CARBONIZING is the name given in the woolen industry to that process by which impurities of a cellulose nature are removed from the wool by first saturating the wool or the fabric with an acid and then drying or baking at a temperature sufficiently high to char and destroy the structure of the impurities, but not so high that the wool fibre itself is damaged. Carbonizing is applied to both raw stock and piece goods. From virgin wool the cellulose impurities that are removed are the burrs or fragments of burrs that have survived the various cleansing and manufacturing processes, and for reworked wool, cotton threads and remnants of cotton linings. Practically speaking, carbonizing is generally applied to woolen goods after weaving, although noils are carbonized as such, but for reworked wool, carbonizing is generally practised while the stock is in the rag stage. Carbonizing is applied either before or after dyeing. If carbonizing is done after dyeing, dyes must be used that will withstand the rigors of the process and if before dyeing the treatment must be such that the goods will take the dye evenly and produce a uniform level shade. As it is a difficult problem to select dyes, particularly mixtures of dyes that will be absolutely unaffected by the relatively drastic treatment of carbonizing, so that goods that were perfectly matched before carbonizing will be perfectly matched afterwards, carbonizing before dyeing is very widely practised. On this account the effect of the carbonizing process on the dyeing properties of the woolen fabric is of much importance for probably half of the piece dye problems arise from conditions incident to the carbonizing process. These problems show up as uneven dyeing of some sort and as the dyer is held responsible, it is obviously to his advantage to know as much as possible of the influences and complications introduced by this process. Some of these troubles, possibly the most frequent, come from not having the goods clean when they are carbonized. If a little soap is left in the goods, and it is surprising how often this happens, this soap is decomposed by the carbonizing acid, and the fatty acid is locally deposited on the fabric. These depositions of fatty acid usually appear as large areas of irregular outline, which when viewed in a strong light or by transmitted light, show darker, although sometimes lighter than the rest of the piece. Cloudiness is a general term applied to such faults if they are not very bad. Skimping on the supply of warm water for rinsing, or rushing the scouring process are the principal causes for leaving soap in the goods, although the quality of the water is likewise of equal importance, and really apt to produce clouds harder to trace to their origin. A lime or magnesia soap coming from hard water is liable to make a particularly bad cloud or blotch. In the writer's observation the clouds from soap left in the goods from insufficient rinsing, are larger in area but show less intense shade difference than those made by a deposited magnesia or lime soap by hard water. The faults of cloudiness attributable to lack of cleansing are fairly easy to trace, although there is one point that must be emphasized and that is an impurity may cause a cloud and then disappear. Listing, shading from side to center and mottled effects may be caused by carbonizing and the fact not recognized or if suspected, because it is only fair to say the dyer always

has the carbonizing process under suspicion, unable to prove the cause or prevent it. To bring such unsolved problems to a minimum, a survey of the principles of physical chemistry involved should be illuminating. There is really not a great deal known of the physico-chemical nature of dyeing itself and some light may also be shed on this subject by considering the principles involved in carbonizing.

While processes have been devised that make use of Hydrochloric Acid in the gas phase, the only two reagents that are generally employed on the large scale are Sulphuric Acid and Aluminum Chloride. When Aluminum Chloride is used the active agent is Hydrochloric Acid.

To Consider the Practical Application of the Carbonizing Process as Applied to Piece Goods

The goods are passed in the open width through an aqueous solution of either of the two agents, Sulphuric Acid or Aluminum Chloride passed through squeeze rolls, and in the most approved apparatus over a suction plate, both of these devices serving to remove excess of solution evenly from the goods, which are then passed still in the open width through and oven or baking dryer chamber where temperatures well above the boiling point of water, but not over 230° Fahr. exist. In regard to temperature it should be noted that temperature and time are mutually variable functions, and as one goes up the other goes down. The British and Continental practice is for lower temperature and longer time than is the present tendency in America. Here it is usual practice to divide the process into three stages, first the removal of excess solution, second a drying and third a short but intense baking. In some cases hydro extracting is used to get rid of excess solution, but this procedure is more likely to result in pieces which afterwards dye unevenly, than where the suction plate or vacuum process is employed. At the elevated temperature of the baking oven, the acid reagents become sufficiently concentrated to avidly attract the water of constitution from the cellulose molecule with resultant charring and disintegration of structure of the cellulose impurities but in the short time allowed not to seriously affect the wool fibre itself. After coming from the oven the goods pass through a mechanical beating or crushing apparatus called dry milling to complete the destruction caused by the acid dehydration, and the goods are then ready to be dyed and finished. The physical chemistry involved then becomes a study of the affect or relationship of various concentrations of acids or aluminum chloride to the wool fibre and how this modifies its dyeing properties. While there have been various observations of the action of acids toward the wool fibre, such duties have not been at all systematic or exhaustive nor in any degree directed with consideration of modern physico-chemical concepts.

Lessons From Leather Chemistry

Fortunately much study has been directed toward the action of acids on hide fibres in the development of modern leather chemistry and the difference between the two animal fibres, those of the hide and those of wool are not so great that much has been learned in leather chemistry may be bodily lifted and applied to the woolen industry.

"Following the pioneer work of Arrhenius, Van der Waale and Ostwald, who while creating the science of physical chemistry, demonstrated the electrical character of chemical reactions, what happens when a salt goes into solution, and the rationale of various forms of chemical activity. The American bio-chemist, Loeb, and the English leather chemist, Proctor, asserted and fairly well proved that there was not an essential difference between protein bodies and the active molecules of ordinary metathetical reactions, except the degree of magnitude. This applies as well to the actually observable organized physical entities such as hide fibres and other protein surfaces as to the large molecular aggregates or micelles of classical colloid chemistry."

Ionization or more exactly the possession of a free electrical charge that attracts ions and therefore promotes chemical combination is not necessarily dependent on solution, but may be and usually is an existent condition that becomes evident when liquids containing free ions come in contact with such surfaces. Despite this immobility, the positive and negative or basic and acidic groups of the protein molecule can form salts with ions of opposite electric charges and such salts are ionized. Due to the restriction of mobility, the fibre itself acts as a cell or chamber surrounded by a semi-permeable membrane and osmotic pressure is developed that swells the fibre. The swelling which may be so great as to cause actual disruption of the fibre is more pronounced with hide fibre in the case of acid solution and with wool fibres with alkaline solutions. The salt forming character or polarity of these protein fibres explain why it is impossible to entirely remove an acid or alkali from combination with the fibre by water alone, but as the acid or basic character of these groups is relatively low, their salts are to a high degree hydrolyzed, so much so in the case of wool as there is always an equilibrium between the water and the acid combined with wool that the quantity of retained acid may by washing in running water be reduced below the point of analytical determination. To prevent the swelling by osmotic pressure of the wool fibre, the most logical procedure is to remove as much of the contained water and incidentally its acidic ions as well by letting the first water the carbonized wool meets, be a saturated solution of a neutral salt.

Rewet with Saturated Salt Solution

For practical purposes, either a solution of common

salt or Glauber's salt should be equally good, but due to a tendency of animal proteins to form additive complexes with chlorides, especially di-basic chlorides, which are likely impurities in common salt, preference should probably be given to Glauber's salt. It may be asked why not remove the acid from the carbonized wool by neutralization. The trouble with this procedure is that the wool fibre is much more susceptible to alkaline swelling than to acid swelling, and while theoretically it might be possible to just neutralize or have the wool slightly on the acid side, practically when there is a large amount of acid present as is the case with carbonized wool, there is always the probability that the large quantity of alkali required to neutralize this, will cause local alkaline swelling before an even distribution was affected. In the early stages of his studies on protein reactions, Proctor noted that while dilute solutions of acids swelled gelatine and hide fibres, concentrated acids and concentrated solutions of neutral salts depressed this swelling. Applying this observation to the carbonizing process, it is apparent in the passage through the saturation acid bath that the wool fibers will be swelled; in the drying, however, the acid in contact becomes concentrated and the swelling will be depressed to a minimum. When the goods are re-wet violent swelling will again take place. Violent changes in the physical character of the wool fibre markedly affect the readiness with which a wool fibre will adsorb dyestuff. Observing how the concentration of the solution in contact with the fibre determines the degree of swelling, the necessity of uniform saturation is apparent and how important it is that the fabric as it goes into the acid bath is clean and free from grease or other substances that may form resist spots. The value of sulphonic acids and agents that hasten penetration in acid solution is likewise evident. When aluminum chloride is used instead of sulphuric acid for carbonizing, the active agent in dehydrating the cellulose impurities is hydrochloric acid. In aqueous solution aluminum chloride hydrolizes to a basic oxychloride and free hydrochloric acid. For the purpose of illustration rather than because it exactly depicts what takes place, the reality is probably more complex, the reaction of hydrolysis may be represented by the following equation:

$$Al\,Cl_3 + H_2O \rightleftarrows Al\,OCl + 2HCl$$

This free hydrochloric acid is taken up by the wool and on drying its avidity for water is sufficient to dehydrate and destroy cellulose. The presence of the aluminum oxychloride will act as a depressant of the swelling of the wool fibre and to a certain degree for this reason there is less danger of uneven swelling and consequent uneven dyeing when aluminum chloride is used than when sulphuric acid is used. On the other hand the degree of hydrolysis is a variable dependent on concentration, which is ever changing, and temperature, so the quantity of hydrochloric acid taken up by the fibre is liable to wide variation and what is gained in one direction may be lost in another. The idea suggests itself that some of the troubles arising from carbonizing might be prevented by using a certain addition of neutral salt with sulphuric acid. Probably if sodium sulphate were used, it would so lessen the avidity of the sulphuric acid for water that much higher temperature than is now employed would be required. If common salt were used results more comparable with aluminum chloride, carbonizing might be obtained, and at less cost. On the other hand there is this difference, the aluminum oxychlorides particularly as they become more basic, tend to become colloidal and thus remain outside of the fibre, while sodium chloride and sulphate, whether ionized or not probably penetrate it freely. Also in solutions containing chlorides in contact with proteins, there is always the possibility of unpredictable and anomalous results, that can only be explained by the assumption of the formation of additive compounds.

In conclusion, we may summarize: researches in leather chemistry show protein fibres combine as a base with acid radicles, that the content of water and concentration of acid in the fibre changes with the concentration of the acid in the external water, and that with these changes the physical condition of the fibre changes, and such changes may be of a magnitude and character to affect the dyeing properties of the fabric, the most rational procedure to keep physical changes at a minimum in addition to securing uniform evaporation or removal of external water, is when this water is replaced by re-wetting the fabric after carbonizing to re-wet with a saturated salt solution.

New General Releases

The General Dyestuff Corporation has issued the following new circulars. Copies may be obtained on request:

1. Benzo Viscose Yellow 5 GL, Benzo Viscose Yellow GGL, Benzo Viscose Orange RL, Benzo Viscose Red BL, Benzo Viscose Violet BL, Benzo Viscose Blue 3GFL. These are rayon colors, said to level well and show no bar effects.

2. Rapidogen Olive Brown IG, Rapidogen Brown IB, Rapidogen Brown IRR and Rapidogen Red IR. All four products are said to be very good as regards fastness to washing and chlorine.

3. Supranol Red PG, PRX, RA and PBX. On woolen material they are said to produce bright reds ranging from scarlet to bluish red. It is further stated that they have very good fastness to water, washing, perspiration and salt water.

4. Benzo Fast Copper Yellow RL, Red RL, and Violet 3RL. It is claimed that the shades so far produced by these colors are fast to light and washing.

New Facts Concerning the Action of Caustic Alkalies on Cotton

By **A. J. HALL, B.Sc., F.I.C., F.T.I.**

For about eighty years the behavior of cellulose, particularly cotton, towards caustic soda and potash has been of fundamental importance to all textile technologists. After treatment with alkali, cotton usually, but not invariably, has an increased reactivity towards most influences and use is made of this fact in the dyeing and finishing of cotton goods. Alkali treatment may also play an important part in the preparation of cellulose in order to render it suitable for conversion into rayon. Recent developments in the manufacture of synthetic resins and plastic materials indicates that cellulose derivatives will play an important part in this rapidly expanding industry, and in the manufacture of these derivatives alkali-cellulose is an important raw material. It thus appears likely that the importance of the alkali treatment of cotton will increase rather than diminish.

RECENTLY three publications dealing with alkali-cellulose have appeared; two of these will most probably have but a limited circulation although they deserve wide publicity because of their value. The new facts now brought forward throw new light on old problems and it is the purpose of this article to consider the more important of the facts disclosed.

Turning first to the acetylation of cotton as in the manufacture of cellulose acetate rayon it might at first be considered that improved acetylation would follow a pre-alkali treatment of the cotton. Curiously enough the reverse is true and, as J. Scheidegger (Dissertation, Technischen Höchschule in Zurich 1931) shows in a special examination of this phase of cellulose reactivity, a mercerized cotton is considerably more difficult to acetylate than ordinary cotton.

This point is of interest not only to manufacturers of acetate rayon but also to finishers of fabric for it must be remembered that during the past two or three years several attempts have been made, particularly by the Sandoz Company, to evolve satisfactory processes for giving cotton fabric a superficial acetylation for the purpose of modifying its absorption of dyestuffs. The general method in such treatments (for example, E. P. 280,493, 314,913, 323,011 and 323,500) consists of padding the fabric with an acetylating mixture, allowing it to lie for several hours, and then washing out the residual chemicals; under these circumstances mono- and di-acetates of cellulose are formed on the fabric surface and they have scarcely any affinity for direct cotton dyes. Obviously it would come into consideration whether or not to mercerize the fabric before such acetylation. The results obtained by Scheidegger suggests that mercerization would certainly have an effect on the acetylation process and most probably an unfavorable one.

In considering the acetylation of mercerized and non-mercerized cotton it must be pointed out that the method of effecting the acetylation has an important influence on the rate and character of this process. For instance, acetylation is assisted by a pre-treatment of the cotton with organic acids so that it makes a difference whether or not the cotton is straightaway immersed in an acetylating mixture consisting of glacial acetic acid, acetic anhydride, and sulphuric acid (catalyst), or first steeped in the acetic acid for several hours and the acetic anhydride and sulphuric acid then added; usually the second method promotes the more rapid acetylation. Also the course of the acetylation is affected by the presence of moisture. It is therefore of interest to ascertain the comparative behaviour of mercerized and non-mercerized cottons under these various methods of acetylation.

Scheidegger in general effected acetylation with the following mixture:

Cotton	20 grams
Acetic acid	80 c.c.
Acetic anhydride	70 c.c.
Sulphuric acid	1.6 c.c. = 3.0 grams

The acetyl content of the resulting products was estimated by treating 2.0 to 2.5 grams with a mixture of 30 c.c. of pyridine and 10 c.c. of acetone and when all the acetate was completely dissolved further adding 30 c.c. of N/1 NaOH. After standing for two hours at room temperature a slight excess of N/1 H_2SO_4 was added and the mixture then titrated with N/1 NaOH using phenolphthalein as indicator. The amount of caustic soda used in the saponification under these conditions is a measure of the actyl content. The acetyl contents (calculated as CH_3. COOH) of cellulose mono-, di-, and tri-acetates are as follows:

Cellulose mono-acetate	29.41% CH_3.COOH
Cellulose di-acetate	48.78
Cellulose tri-acetate	62.51

The degree to which cotton enters into the acetylation process may be judged by the rate at which the temperature of the reaction mixturer rises. In Fig. 1 are shown the temperature curves for ordinary cotton with and without pre-treatment with acetic acid; it is obvious that the pre-treatment with acid much assists the acetylation. Mercerized cotton is equally susceptible to such acid pre-treatment.

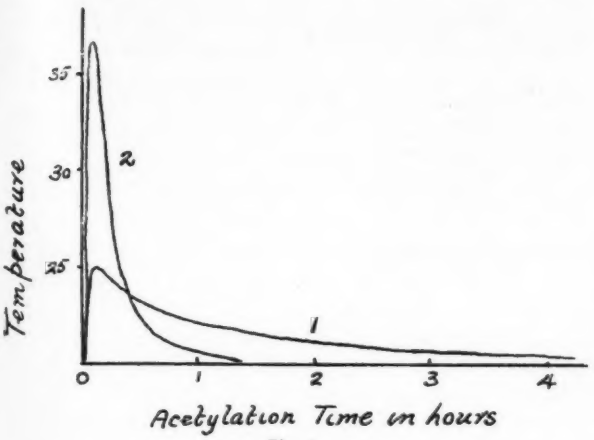

Fig. 1
1. Temperature curve in ordinary acetylation. 2. Temperature curve in acetylation after acid pre-treatment. The curves were obtained with ordinary cotton having a moisture content of 5.85%

The moisture content of the cotton also affects the acetylation process and in Fig. 2 are shown the temperature curves for both types of acetylation using ordinary cotton having increasing initial moisture contents; the greater the moisture content the more energetic is the acetylation reaction. Similar results were obtained with alkali-treated cotton.

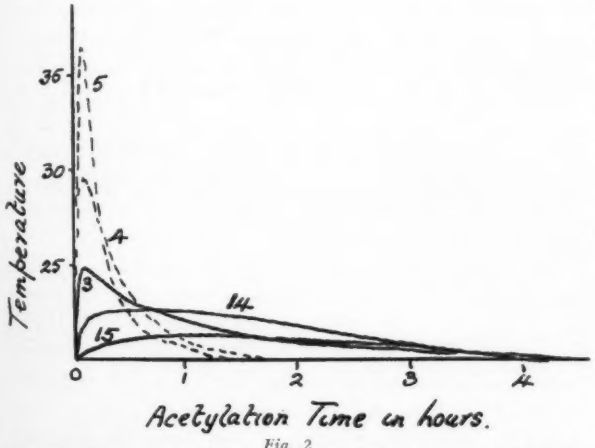

Fig. 2
15. Temperature curve in ordinary acetylation with cotton having 0% moisture. 14. Temperature curve in ordinary acetylation with cotton having 2.9% moisture. 3. Temperature curve in ordinary acetylation with cotton having 5.85% moisture. 4. Temporary curve in acetylation after acid pre-treatment with cotton having 0% moisture. 5. Temperature curve in acetylation after acid pre-treatment with cotton having 5.85% moisture.

A series of samples of cotton were treated for two hours with caustic soda of increasing concentration at 20°C. and 95°-100°C. then freed from alkali by washing with water, dried at 70°-80°C., conditioned in air for two hours, and afterwards acetylated with and without acid pre-treatment. The temperature rises in the acetylation mixtures were noted and the results shown in the curves in Fig. 3.

It is noted that a hot alkali treatment has much less effect than when cold alkali is used. In the case of cold alkali the temperature attained in acetylation gradually diminishes as the alkali concentration increases and the effect

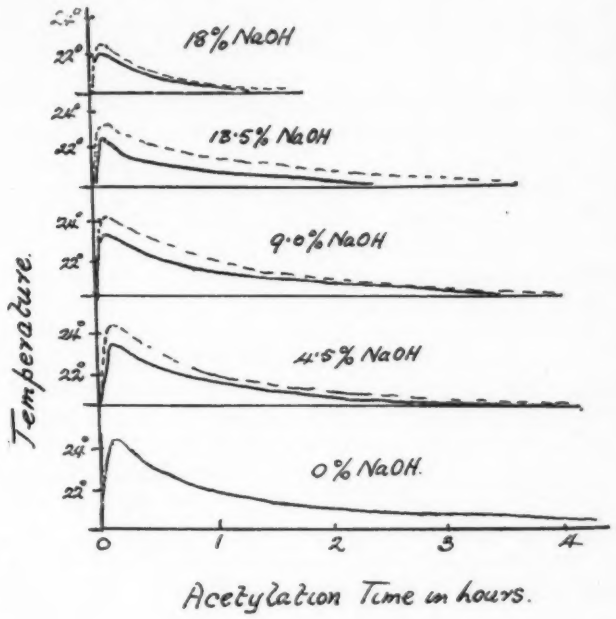

Fig. 3

is noticeable when but 4.5% caustic soda is used. On the other hand, although the same effect is noticed with hot alkali the treatment does not appreciably affect the temperature rise during acetylation until 13.5% caustic soda is employed.

The hindering effect of the alkali treatment in acetylation is also clearly observed when the cotton is afterwards pre-treated with acid.

But not only does the temperature of the acetylation mixture rise less in the case of alkali-treated cotton; the degree of acetylation is also decreased. The following results clearly show this.

Treatment	*% Acetyl content of product* (after 8 hrs. acetylation)			
	4.5%	9.0%	13.5%	18.0% NaOH
Cold alkali.	Fully acetylated		27.1	16.3
Hot alkali.	Fully acetylated		58.7	21.4
Cold alkali.	Fully acetylated		51.1	41.2
(followed by acid pre-treatment)				
Hot alkali.	Fully acetylated			44.7
(followed by acid pre-treatment)				

It is noted that full acetylation may be obtained with cotton treated with *hot* 13.5% caustic soda if this is followed by treatment with acetic acid before acetylation. The acid treatment thus has the effect of counter acting the adverse results of the alkali treatment.

The acid pre-treatment of ordinary cotton facilitates subsequent acetylation and it is noticed that the maximum effect is obtained when the cotton is in contact with the acid for *one* day at ordinary temperature. In contrast to this it is found that the full effect of the acid treatment is not obtained unless the mercerized cotton is in contact with the acid for *three* days. Even after the full acid

pre-treatment mercerized cotton does not acetylate in the same manner as ordinary cotton for it is noticed that with the mercerized cotton the acetylation mixture remains cloudy due to the presence of undissolved fibres while the mixture soon becomes quite clear in the case of ordinary cotton.

Special significance must be attached to the opposite effects on acetylation as produced by acid and alkali treatments. In this connection attention must be drawn to some investigations of Malm and Clarke (J. Amer. C. S., 1929, *51*, 274) relating to the acetylation of ordinary and mercerized cottons by immersion in boiling acetic acid. Acetylation with acetic acid alone is very difficult (the use of acetic anhydride is required) but after prolonged treatment it was found that ordinary cotton formed the acetate having the composition, $C_{24}H_{39}O_{19}(OC.OCH_3)$ (acetyl content, 8.69%) and mercerized cotton, $C_6H_9O_4(OC.OCH_3)$ (acetyl content, 29.4%) and this result appears in contradiction to those of Scheidegger.

Actually there is an essential difference between the investigations of Scheidegger and those of Malm and Clarke in so far as in the first, the cotton is dissolved in the acetylation mixture while in the latter the cotton retains its original fibrous form. But a more subtle difference has been brought forward by Scheidegger and he has been able to show that although when the partially acetylated ordinary and mercerized cottons (acetylated by immersion in boiling acetic acid as in the Malm and Clarke investigations) are further acetylated in the usual

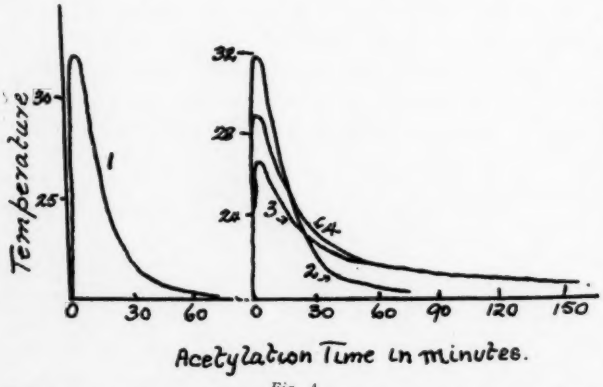

Fig. 4
Temperature curves of ordinary and mercerized cottons during acetylation after a pre-acetylation in boiling acetic acid. 1. Ordinary cotton after pre-acetylation for 4 to 48 hours. 2. Mercerized with an after pre-acetylation for 24 to 48 hours. 3. Mercerized with an after pre-acetylation for 4 hours. 4. Mercerized with an after pre-acetylation for 8 hours.

manner the acetylation of the ordinary cotton (partially acetylated) is more energetic than that of the mercerized cotton (partially acetylated); the curves in Fig. 4 illustrate this excellently. Furthermore the viscosities of the resulting cellulose acetates are considerably smaller in the case of the mercerized cotton. It is therefore concluded that acetylation with a mixture of acetic acid, acetic anhydride, and sulphuric acid, is quite a different reaction from the acetylation with boiling acetic acid alone; particularly it is considered that the difference mainly lies in the hydrolytic effect of the acid on the cotton in the latter type of acetylation. Thus it must not be considered that the results of Scheidegger, and Malm and Clarke are contradictory. Support for this may be obtained in several directions for it has been frequently observed that any acid treatment of cotton such that it is partially degraded assists its subsequent acetylation.

The following viscosity measurements are of interest because they show how the viscosity of cellulose acetate is intimately dependent on the process of acetylation:

Acetylation conditions	*Viscosity*
1. *Ordinary cotton.*	
Usual method of acetylation at a temperature not exceeding 25 C. using as catalyst	
(a) 15% of Sulphuric acid.....	4500 — 5600
(b) 30% of Sulphuric acid.....	314
2. Method of acetylation after acid pre-treatment of cotton with cold acetic acid. Catalyst, 15% sulphuric acid. Maximum acetylation temperature:	
(a) 35 C.	1210 — 1350
(b) 5 C.	37600
Mercerized cotton	
As 2 (a).	690 — 786

It would appear that the effect of mercerization on cotton as revealed by acetylation processes consists of a diminution in the size of the cellulose micellae. Since alkali treatment definitely has the effect of hindering subsequent acetylation it must be concluded that in the manufacture of cellulose acetate rayon much depends on the alkali boiling processes used for purification of the cotton and these should therefore be very carefully controlled.

Viscose rayon has been stated by Hagenbuch (Helv. Chim., 1930, *13*, 566) to be more resistant to acetylation than is mercerized cotton.

The second series of investigations concerning the action of alkalis on cotton to which reference must be made are those of A. Rhomberg (Dissertation: Technischen Höchschule zu Stuttgart). In the first place, Rhomberg sought a method by which the degree of mercerization produced by alkali treatment could be accurately and conveniently measured. For this the various methods known for this purpose were reviewed and carefully tested. Among these were the zinc chloride-iodine reagent of Lange (Chem. Zeit., 1903, *27*, 735), the Congo Red dyeing test of R. Haller (Textilber., 1926, *7*, 65), the browning test of Kauffmann and Waldinger, and certain reactivity methods in which the sensitivity of alkali-treated cotton to oxidation with bromine water, hydrogen peroxide, and sodium hypochlorite is made use of. Finally, it was concluded that the most satisfactory method is that in which the mercerized cotton is heated under specified conditions with sulphuric acid and then tested by the Kauffmann permanganate method.

The acid treatment is carried out by steeping one gram of the alkali-treated cotton in 200 c.c. of 15% sulphuric acid at 40° C. seven hours (in a thermostat-controlled

(Continued on page 594)

Proceedings of the American Association of Textile Chemists and Colorists

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* * *

Meeting, Philadelphia Section, Sept. 30.

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Proceedings of the American Association of Textile Chemists and Colorists

Physical Chemistry As An Aid to the Textile Industry*

By **PROF. E. K. STRACHAN**
Brown University

CHEMISTRY as a science grows so rapidly and is so intricate that those who are engaged in the practice of chemistry as a useful art find it rather difficult to keep up with the newer advances of the subject, and fully as hard perhaps to retain the fundamentals they learned in school. It is because of this that your committee has asked me to talk to you on Physical Chemistry. So then, if I may present a brief review of a few of the things that I think are essential, perhaps it will serve to bring back to the upper layers of your consciousness some topics in physical chemistry which now lie dormant in your minds, with the hope that it may cause you to see the things you are doing every day in a new light, or it may suggest a different method of attacking some problem that troubles you.

The particular things that I want to talk about are first of all chemical equilibrium, particularly in its application to electrolytes, and later I should like to talk briefly on colloid chemistry in its relation to the textile industry. These are tremendously large subjects and I can only present a small part of them and hope to be suggestive rather than exhaustive.

When discussing these subjects first I should like to bring to your attention the matter of chemical equilibrium, and I shall try to speak to you the same as to a class in college. Let us consider the chemical reaction, a mols of substance A combine with b mols of substance B to give m mols of substance M and n mols of substance N:

$$aA + bB \rightleftharpoons mM + nN$$

We can show that the concentration of substance M raised to the mth power, multiplied by the concentration of substance N raised to the nth power, divided by the concentration of substance A to the ath power and the concentration of B to the bth power equals a constant:

$$\frac{C_M^{\,m} \times C_N^{\,n}}{C_A^{\,a} \times C^{\,b}} = K$$

We can prove this by experiment, and we can also prove it in an entirely different way on the basis of the kinetic theory of reaction velocity, and in a third way from the law of conservation of energy and the law of degradation of energy. These methods of proof all lead to the formula before you. Take for example a simple reaction,—alcohol combines with an acid to form an ester, ethyl acetate perhaps and water. Now we can write that the concentration of ester (ethyl acetate) multiplied by concentration of water and divided by the concentration of acid (acetic acid) and the concentration of alcohol equals a constant, which constant has been found by experiment to be 4 at 25°C.

$$\frac{\text{C ester} \times \text{C water}}{\text{C acid} \times \text{C alcohol}} = K = 4 \text{ at } 25°\text{C.}$$

This is a reversible reaction—ester and water if allowed to react will form alcohol and acid, until the reaction mixture reaches the equilibrium proportions of acid, alcohol, ester and water. Suppose we mix an equal number of mols of acid and alcohol and desire to know how much ester will be formed. We get our answer very simply by the following computation:

Let X = mols ester = mols water
1 — X = mols alc. = mols acid

If X equals mols of ester, it is a necessary consequence of our chemical reaction that X will also equal mols of water, and if I start with 1 mol of acid, then 1 — X is going to be the mols of alcohol left and is also going to be the mols of acid left at the end of the chemical reaction.

$$\frac{X \quad X}{(1-X) \quad (1-X)} = 4, \text{ or } X = 2/3 \text{ mol ester}$$

You can often judge the efficiency of a process and whether or not you are getting your process as efficient as is possible by use of this law. Take a simple example thus: Suppose the alcohol happens to be the expensive ingredient, then, to produce ester as efficiently as possible, we should use up all of the alcohol we can. Now, if we increase the concentration of acid we must decrease the amount of alcohol left over when equilibrium is attained. How much acid should we add for 90% utilization of the alcohol? Again we will start our calculations with 1 mol of alcohol and we now use y mols acid. At the end of our reaction we must have 90% alcohol converted to ester. Then we have 0.9 mols of ester and 0.9 mols of water and only 0.1 mol of alcohol remaining, and we will have Y—0.9 acid, and that again must equal the constant 4.

*Paper presented before the R. I. Section (April 29, 1932).

$$Y = \text{mols acid per mol alcohol}$$

$$\frac{0.9 \times 0.9}{(Y-0.9)\ (0.1)} = 4$$

When we solve this equation we find that Y = 2.9. Then, in order to get 90% utilization of alcohol you use pretty nearly three times as much acid as alcohol. To get a bigger yield we can use more of the inexpensive substance, but not, of course, using so much of it that the cost of the less expensive exceeds the saving of the more expensive one.

There are various ways of getting a bigger yield: First, increase the concentration of one reagent. Second, decrease the concentration of one product or remove it from the reaction mixture. This latter principle applies very aptly to the sulfonation of benzol. (The formation of benzol sulphonic acid is the first step in the manufacture of phenol). If benzol and sulphuric acid are allowed to react, benzol sulphonic acid is formed until the strength of the sulphuric acid is reduced to about 80%, when the reaction stops. The happy idea of removing one of the products of reaction eliminates this difficulty. The benzol vapors are blown through hot sulphuric acid and in that way the water is removed as fast as it is formed and practically complete utilization of the sulphuric acid occurs while the vapors are condensed and the excess benzol recovered for further use. We frequently remove a product of reaction by precipitating it. The third method of increasing yield is by means of pressure. The effect of pressure on a reaction is such as to make the equilibrium go toward the formation of the substance that occupies the smallest volume. If we consider for example, the preparation of ammonia from nitrogen and hydrogen, 1 mol of nitrogen and 3 mols of hydrogen combine to form 2 mols of ammonia. You can see at once we have 4 mols of gas initially, and two mols at the end of the reaction. $N_2 + 3H_2 = 2NH_3$. Or by the gas laws, 4 volumes to begin with and 2 volumes of product. Since the product occupies the smaller volume, increase of pressure will favor the reaction. The fourth method of increasing yield is the effect of temperature. An example of that might be ammonia synthesis. With this reaction a considerable amount of heat is evolved.

$$N_2 + 3H_2 = 2NH_3 + 10950 \text{ calories}$$

Increase of temperature decreases the yield of ammonia. Another example is the dissociation of water to form hydrogen gas and oxygen gas, which reaction absorbs heat.

$$2H_2O = 2H_2 + O_2 - 58700 \text{ calories}$$

The higher the temperature the greater the tendency for the water to break down into oxygen and hydrogen. The equilibrium will be forced in the direction of the absorption of heat. This is the Van't Hoff LeChatelier principle. Increase of temperature increases the yield of those reactions that absorb heat and decreases the yield of those that emit heat. Or increase of temperature displaces the equilibrium in the direction accompanied by absorption of heat.

The mass action law we have been discussing is very useful in dealing with equilibria in solutions of electrolytes. Let an acid be represented by the symbol HA, in which H is the hydrogen and A the acid radical. This dissociates to form hydrogen ion and acid ion, as we all know. The mass action law can be applied in the following form:

$$HA = H^+ + A^-$$

$$\frac{C_{H}{}^+ \quad C_{A}{}^-}{C_{HA}} = K,$$

in which $C_H{}^+$ is the concentration of hydrogen ion, $C_A{}^-$ the concentration of acid ion, and C_{HA} the concentration of acid which remains undissociated, while K is the equilibrium constant and is commonly called the ionization constant of the acid. The constants vary from one acid to another. The more highly dissociated an acid is, the stronger it is, and it follows as a simple matter of arithmetic that its ionization constant will be greater the stronger the acid is. If we need stronger acid for some process we are operating, we choose one with a greater ionization constant, and vice versa if we desire a weaker acid we select one of smaller ionization constant. By looking about we can find acids of practically any value of the dissociation constant we desire. From this it can be seen that formic acid is ten times as strong as acetic. The following offer further examples of the ionization constants of acids:

Propionic acid	1.45×10^{-5}
Mono Chlor Acetic	1.55×10^{-3}
Di Chlor Acetic	5×10^{-2}
Tri Chlor Acetic	3×10^{-1}
Lactic Acid	1.38×10^{-4}

In general the mineral acids are strong and the organic acids are weak, but this is not a rigid rule by any means for the strongest organic acids in this list are far stronger than many of the weak mineral acids.

Carbonic acid exhibits an interesting two-stage dissociation. Carbonic acid dissociates into 1 hydrogen ion and 1 bicarbonate ion, which latter again dissociates into 1 hydrogen and 1 carbonate ion, thus:

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3{}^-$$

$$HCO_3{}^- \rightleftharpoons H^+ + CO_3{}^=$$

We can write ionization constants for each dissociation. In other words under the bicarbonate ion $HCO^-{}_3$ behaves like an independent acid. The ionization constant of the first hydrogen ion is usually called the K_1 constant, that of the second hydrogen, the K_2 constant; carbonic acid, therefore, has two ionization constants:

$$K_1 = 3.5 \times 10^{-7}$$
$$K_2 = 4 \times 10^{-11}$$

Phosphoric acid dissociates in three stages and has three constants:

Phosphoric Acid $K_1 = 10^{-2}$
$K_2 = 2 \times 10^{-7}$
$K_3 = 3.6 \times 10^{-13}$

This discussion of the strength of acids and their ionization constants leads us to a consideration of buffer solutions. A buffer solution is one that can take up a considerable amount of acid or alkali without changing its hydrogen ion concentration appreciably. Buffer solutions are composed of a weak acid and one of its salts. We will examine the equilibrium equation again. The concentration of hydrogen ion and the concentration of acid ion, divided by the undissociated acid, equals a constant.

$$HA \rightleftharpoons H^+ + A^-$$
$$\frac{C_{H^+} \times C_{A^-}}{C_{HA}} = K$$

Sodium acetate added to such a solution would dissociate to form sodium ions and acetate ions. We can cause this equilibrium to run to the left by increasing the concentration of any substance on the right. If we increase the concentration of acetate ions, e.g., by adding sodium acetate, the reaction can be forced to the left and the concentration of hydrogen ions decreased. Hydrogen ions will combine with the acetate ions and form more undissociated acid. Suppose we have a mixture that is N/10 acetic acid and N/10 sodium acetate. The hydrogen ion concentration of such a solution is equal to the ionization constant of acetic acid (1.8×10^{-5}) multiplied by the concentration of undissociated acid and divided by the concentration of acetate ion. On solving the preceding equation for concentration of hydrogen ion it appears that

$$C_{H^+} = \frac{1.8 \times 10^{-5} \times C_{HA}}{C_{A^-}}$$

If we substitute the numerical data we find that

$$C_{H^+} = \frac{1.8 \times 10^{-5} \times 0.1}{0.1 \times 0.86}$$

or,

$$C_{H^+} = 2.09 \times 10^{-5}$$

If we compute the hydrogen ion concentration of N/10 acetic acid we find that it is 1.35×10^{-3}. The addition of sodium acetate reduced the acidity of that solution to about 1/60th. In a qualitative way this principle has been used for a long time in the dyeing of certain dyes. Suppose an acid dye is being dyed from a sulphuric acid bath. The addition of Glauber's salt will reduce the hydrogen ion concentration and hence the speed of dyeing. To an acetic acid dye bath you add sodium acetate when you want a slow dyeing mixture. You lower the acidity by putting sodium acetate in the solution.

I am going to take just a few moments to refer to amphoteric substances. An amphoteric substance is one that may act as an alkali or an acid, depending on surrounding conditions. Let us take as an example an amphoteric substance that is closely allied to protein bodies such as wool, silk and other animal fibers. I refer to amino acetic acid, NH_2CH_2COOH. This compound will react with an acid to form a salt, e.g., $ClNH_3CH_2COOH$ or it will combine with a base likewise forming a salt, e.g., NH_2CH_2COONa. One end of the molecule is an acid and the other a base.

Now one end of such an amphoteric molecule may be more strongly basic than the other end is acid. If we alter the alkalinity of the solution we increase or decrease the hydrogen ion concentration and so may force back this dissociation of one end of the molecule or the other until it reacts neither acid nor alkaline. The hydrogen ion concentration at which a substance is just as much dissociated on the acid end as on the basic end is called the iso-electric point. The substance, under these conditions, referred to in terms of dyeing, is just as capable of taking up an acid as a basic dye. It has been shown many times that if we plot horizontally the hydrogen ion concentration and vertically the percentage exhaustion of the dye bath, when applying an acid dye to wool or silk, we obtain a curve (No. 1 in the figure) showing how the per cent exhaustion falls off with decreasing hydrogen ion concentration, going down to almost nothing. Curve No. 2 shows how the per cent exhaustion increases with decreasing hydrogen ion concentration when applying a basic dye to the same fiber.

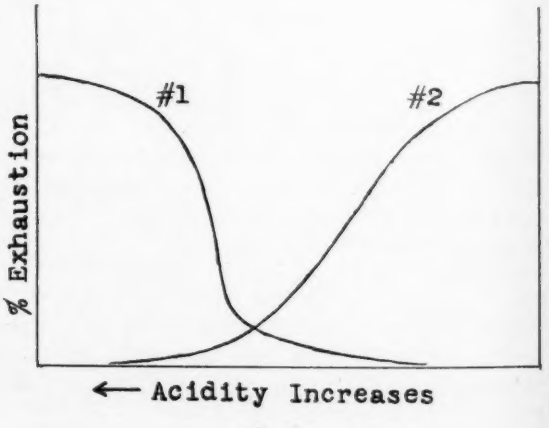

Fig. 1

These curves across at a hydrogen ion concentration very near the iso-electric point of the fiber.

Quite a number of studies have been made of this phenomenon of iso-electric point. It is intimately con-

nected with many of the physical properties of colloidal substances, particularly the extent to which they swell in water and salt solutions. We are not only concerned with the dyeing of fibers, but with a great many of their physical properties which cause swelling in water and other fluids, and these are closely allied to the iso-electric point and colloid character. Gelatin is one of the most favorable substances on which to work. The swelling, viscosity, adsorption and many other of its properties are determined by the iso-electric point and by the hydrogen ion concentration of the solution, as well as by the properties of the substance which is being adsorbed. It is interesting to note that wool and silk have adsorption properties similar to gelatin, while the adsorption properties of agar are similar to those of cotton. Consequently it would be interesting from the point of view of the textile chemist to know more about the behavior of agar.

There is one other topic that I want to mention and that is the matter of reaction velocity. In the diazotization process we are more concerned with the reaction velocity than with equilibrium. This too depends on hydrogen ion concentration. I have not time to go into all the advances that have been made in the study of accelerators or catalysts. Not so many people are aware of the extent to which the negative catalysts or inhibitors are coming into prominence. For example, if 1 part of hydroquinone is added to 40,000 parts of linseed oil the linseed oil will not dry. There are quite a number of other inhibitors. The matter of inhibitors in dyeing is a subject of tremendous importance to the textile industry. Some of these have been known for at least fifteen years (some of you will probably say forty-five years). The new Rapidogen colors involve the use of a negative catalyst—something that will inhibit the reaction or stop it until you are ready to dye. We are indebted to the rubber industry for the development of many of the inhibitors.

Inhibitors also have their use in acids to prevent the acid from attacking metal. I heard of one plant where they ran hydrochloric acid, in which was incorporated an inhibitor, through their iron pipes which were covered with ironrust. The ironrust was completely removed and it was claimed that the acid had no effect on the iron pipes.

I should like to bring to your attention by means of a simple experiment the fact that the electric charge on a substance has a great deal to do with dyeing. The reaction of sodium chloride with silver nitrate to form sodium nitrate and silver chloride can be conducted in such a way as to produce either positively or negatively charged colloidal silver chloride. If silver chloride is precipitated with an excess of sodium chloride, as was done in the flask I now show you, it will be negatively charged and will be dyed with the basic dye that I have added as you can readily see. On the other hand, if an excess of silver nitrate is present the silver chloride will be positively charged and will show an affinity for acid dyes as is apparent from the examples which I now exhibit.

Discussion

Q. Explain something about alkali reactions with cotton.

A. Cotton is not an amphoteric substance. It does not have an iso-electric point and having neither acid nor basic properties, it is not at all comparable with silk or wool. As you probably know, the usual method of proceeding with cotton, if not using a direct color, is to apply a mordant which will be quite analogous to the adsorption of negative ions on the surface of the cloth. Cotton will then take up basic substances. Adsorb on cotton a positive substance similar to chloride ions and then cotton can take up an acid dye.

Q. How about dyeing vat colors?

A. That is possibly plain adsorption. There are many substances that of themselves appear to be neutral. Platinum cannot be dissociated, yet platinum, when finely divided enough, will assume an electric charge. To a certain extent the surface layer of cotton has some electric charge on it. There are, however, adsorption phenomena which have no apparent connection with electrolytic ionization. Take, for example, the way chalk sticks to the blackboard. If you go into a mill and examine the beams you will notice that they are covered with dust, the bottom being covered as well as the top, the finer particles being on bottom. Dirt in cloth exists in very fine particles and the problem frequently is to find something that will displace these fine particles of dirt. Soap has a greater affinity for the cotton than the dirt has. That is what we call selective adsorption. Take a perfectly clean piece of metal, put in water and then draw it out—the water flows smoothly on the metal. Put it back in the water and put in a drop of turpentine—the turpentine forces itself down on the metal as it has a greater affinity for the metal than the water has.

Q. Have you any suggestions for the control of alkalinity where using caustic and hydrosulphite?

A. The glass electrode has been used, but this was not 100% satisfactory. This is a very important point to settle.

Q. Is there any evidence of dissociation of vat colors in the leuco state?

A. I think that most of the vats when reduced to the leuco are in the form of their sodium salts and dissociate.

Q. The concentration of the alkali would mean a great deal in the dissociation of the substance?

A. I should suppose so.

Q. An argument started in the plant the other day in regard to the salting out of vat colors. We were working with a mixture of jade green and yellow, and we found that the green went on much faster and exhausted better than the yellow. The person to whom I was talking claimed that adding salt to the bath would speed up exhaustion of the yellow without having any appreciable effect on the green. Is this correct?

A. It is quite possible that your information is correct. It is quite possible for the salt to accelerate one color more than another. Then there is another consideration, too, when dyeing two colors, one may have more affinity for the fiber than the other, and as one goes on the other comes off.

Q. Do the inhibitors belong to any general class of substance?

A. There is no definite class. Nitrogen bases in general inhibit the action of acids on metals. Acetanilid inhibits the decomposition of hydrogen peroxide. The dihydroxy phenols have been used as inhibitors for oxidations of organic materials. If you find one type of compound that acts as an inhibitor for a certain type of reaction you will find that similar compounds will also react to a greater or less extent in the same way.

Q. In the case of linseed oil, if you add an inhibitor to slow up the drying of the oil, is it not also possible that there is some other substance the addition of which would speed up the drying of the oil?

A. The cobalt resinates, maganese resinates and many other substances exhibit this effect.

Q. What are the retarding agents in the Rapid Fast colors?

A. I don't know, although I have heard of ethylene glycol being used. I really don't know.

SEPTEMBER MEETING, NEW YORK SECTION

THE first meeting of the New York Section for the 1932-1933 season was held at the Chemists' Club, 52 East 41st Street, New York City, on Friday evening, September 23rd at 8 P.M. Preceding the meeting an informal dinner was held at 6:45 P.M. The speakers were: D. H. Jackson of the Croll Reynolds Company whose subject was "Vacuum Refrigeration for the Textile Industry"; and C. F. Chandler of the Acele Division, E. I. duPont deNemours & Co., who spoke on "Properties of the Acele Yarns in Regard to Dyeing and Finishing." Open discussions were held following the presentation of each paper. A complete stenographic report of the proceedings of the meeting, including the papers as presented and the resultant discussion will appear in an early issue of the Reporter.

STANDARD SILK SAMPLES

There have been prepared, under the direction of the Sub-Committee on Fastness of Dyed Silk, standard dyed silk fabrics to represent four classes of fastness to washing—namely, Class I, Class II, Class III and Class IV. These standards have been carefully dyed with the dyestuffs and according to the dyeing methods recommended in the 1931 Year Book.

The A. A. T. C. C. is prepared to furnish sets of these washing standards for a nominal charge which will cover the cost of preparation. It will be possible to accurately grade the fastness to washing of any dyed silk fabric by comparing it with the standards after subjection to the standard washing tests approved by this Association. All inquiries concerning these Silk Washing Standards may be addressed to the Chairman of the Research Committee,

Louis A. Olney,
Lowell Textile Institute,
Lowell, Massachusetts.

ASSOCIATION BADGES

The lapel button badge illustrated herewith is worn by members of the American Association of Textile Chemists and Colorists.

The three "rings" are enameled in red, yellow and blue, respectively, and the initials and border are brought out in gold. The general effect is exceedingly attractive.

Badges may be secured at $1.50 each by addressing the Secretary.

A. NEWTON GRAVES,
Franklin Process Co.,
Providence, R. I.

AMERICAN DYESTUFF REPORTER

Devoted to the use and application of dyestuffs and the mechanical equipment incidental thereto

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PROFIT ON IMPORTED DYES

THAT there is still a profit to be made on imported dyes is shown in a special bulletin of the Synthetic Organic Chemical Manufacturers Association. The facts therein are obtained from the Report of the U. S. Tariff Commission to Congress on the investigation in compliance with Section 340 of the 1930 Tariff Act. As applied to coal tar dyes the investigation brought out the following facts.

The investigation apparently covered slightly more than 4,500,000 pounds of the 11,000,000 pounds imported from July 1st, 1927 to June 30, 1929, 54.5 percent of which were non-competitive and 45.5 percent were competitive. In quoting the special bulletin of the Association we read the following:

"The unit sales value of imports was $2.10 per pound, whereas the unit invoice value taken from import bulletins for this same period was 81c per pound.

"We have previously estimated that the sales value of the dye imports was about twice the invoice value. It is apparent now that we were modest. The actual sales value was nearer two and one-half time the invoice value. On this basis, and assuming domestic consumption to have been domestic reported sales, minus exports and plus imports, we arrive at an apparent domestic consumption of a little over 148,000,000 pounds of dyes for the two years in question with a total sales value of $92,000,000 of which 11,000,000 pounds were imports with a sales value of a little over $23,000,000, showing that imports supplied about 7.5% of the domestic consumption and about 25% of its sales value.

"The unit invoice value of 81c plus a duty of 64c as against a $2.10 unit sales value must have shown a satisfactory margin to the importers."

HELPING THE UNEMPLOYED

THE recent announcement of the Forstmann Woolen Co., regarding the fact that it would go on a five day week schedule in order to increase the number of persons employed, is worthy of comment. In the near future, with the opening of the new seasonal lines of woolens, the company will introduce throughout their mills the two shift working schedule already in use in some of the departments in order to further distribute the amount of available work amongst a greater number of workers. These two shifts operate for five days a week with the first shift running from six A.M. to two P.M. and a second shift from two P.M. to ten P.M. It is expected that the new program will increase the number of workers by a minimum of ten per cent, and a further increase is anticipated when the late winter and spring fabrics are introduced.

Of further significance in the same announcement is the second part of the same plan which entails a complete modernization of the buildings and equipment. This phase of the program has furnished employment for many workers other than in the textile line.

Whether the plan as announced will become a permanent policy or merely a temporary emergency measure will depend upon the success of it in operation. Whether we are definitely on the way to business recovery or whether prosperity is still more or less to be conjectured is probably not yet clear, but the adoption of such policies as mentioned above will surely tend to hasten such recovery.

A RESULT OF RESEARCH

THE fact that there is, and has been, extensive research work being conducted in the textile industry was shown by the recent introduction of a new anti-crease finish after fourteen years spent in studying the problem. This anti-crease finish for cottons, rayons and silks has been developed by Tootal, Broadhurst Lee Co., Ltd., a British firm, and it is now believed that negotiations with domestic finishers will be completed within a month providing for the introduction of this finish in this country in the late spring lines.

This is rather an important development and much interest among mill men and converters in this country has been shown. It is of significant importance to those firms engaged in the handling of rayon crepes inasmuch as the tendency to wrinkle as shown by these fabrics has long been a cause of dissatisfaction. It is also important to those handling cotton dress goods who, incidentally, are said to believe that 1933 will show an increased demand for novelty cotton fabrics. According to the *Journal of Commerce*, it is believed that reducing the tendency of cotton dresses to wrinkle to a minimum and in this manner cutting the cost of upkeep of cotton frocks would add considerably to their popularity.

It has been announced that the process is already in use in England and by way of introduction it has been planned to place a line of ties on the market in that country treated with the anti-crease finish, believing that it would be a good means of bringing the attention of the public to the value of the process.

The fact that it was a real research problem is illustrated in a statement by the research department regarding the development of the process. It follows in part:

"Here is a piece of cotton cloth. Crush it in the hand and throw it on the table; it is covered with creases. Here is a piece of woolen cloth; treat it similarly and it shows scarcely any creases. Make cotton like wool in this respect.

"This was worse than looking for the proverbial needle in the bundle of hay. One does at least know that the needle is there, but it was not certain that cotton could be endowed with the requisite woolen property.

"Initial difficulties soon appeared. The newer industries, like the electrical, had originated in and owed their rapid development to research, but the old and well established ones, such as those concerned with textiles, owed their technical progress mainly to inventions of machines, and little, if any, research had been done on the physical properties of the materials used, consequently there was no large volume of fruitful literature in which to search for guidance.

"For fourteen years the problem has been worked on, but it is only recently that a satisfactory solution has been found and patented, which, while making cotton fabrics springy, maintains their other textile properties.

"During the progress of the work much fundamental research has been necessary. While this has assisted in the solution of the main problem, it has also suggested others which have been solved and the results incorporated in technical practice, this justifying the view that research can make useful contributions even in such an old industry as that of cotton.

"At an early stage it was found that if springiness of the fabric as a whole is to be produced, each individual cotton hair must be endowed with the necessary property. Hence the elastic qualities of cotton hairs had to be investigated. In the engineering industries the properties of materials are thoroughly tested in the laboratory before they are built into structures, but the published literature gave little information on the cotton hairs from which all cotton fabrics are built. Hence new methods had to be invented and novel testing machines built for the purpose."

The statement continues to show the actual working out of the problem. What is quoted above shows that it was a real problem and involved a great deal of true scientific research. The actual importance of the results obtained will be shown in forthcoming adaptations of the process involved. It does show one thing very plainly, and that is, that some firms are willing to expend time and money on textile research, believing that the results obtained will repay them for their efforts.

Houghton Exhibit

In view of the expanding business of the textile trade this fall, E. F. Houghton & Co., Philadelphia, Pa., manufacturers of textile soaps, softeners and other processing materials, as well as special textile lubricating oils and leather products, will have a larger exhibit than ever before at the Southern Textile Exposition.

They will show for the first time several new processes developed by the Houghton research staff which will be of particular interest to southern textile men. One of these is an entirely new process known as the Raylubric Process for throwing rayon crepe. This process consists of a cream type softener plus a sizing material which is used in making up a soaking bath in which the rayon is soaked for 20 to 30 minutes before being thrown. It has proven a very economical and simple process and produces a rayon crepe of unusual merit.

They will also exhibit for the first time several new types of finishes for cotton goods which will be of interest to every cotton cloth manufacturer.

Among the other products which they will exhibit at the Southern Textile Exposition are hosiery boil-off agents, dyeing assistants and softeners.

Solophenyl Fast Blue Green BL

This is claimed to be the fastest to light direct dyeing green for cotton and rayon available today. It is said to be level dyeing. It is further claimed that it has good solubility and fastness to alkali, acid, rubbing, ironing, sulphur and sulphur dioxide fumes; besides showing good fastness to perspiration, salt water, vulcanizing and having good water and wash fastness.

The brightness of its shade is said to facilitate its use as the Blue component of Kelly and Jade Greens and as the Blue element in any fast direct dyeing combination in which extreme fastness to light is required.

In combination with it, no other types are suggested by the manufacturer than—

Diphenyl Fast Yellow GL, GCX and B
Diphenyl Fast Red 5GL
Diphenyl Fast Rubine RL
Diphenyl Fast Violet C4B
Diphenyl Fast Blue BL Conc.

for all general purposes, and Diphenyl Chlorine Yellow FF, a product which is not dischargeable and should be used with discretion.

In the case of Jade and Kelly Greens, the manufacturer states that Diphenyl Fast Yellow GCX should be employed for it combines not only fastness comparable with the Solophenyl Fast Blue Green BL, but is dischargeable as well.

Circular No. 848, issued by the Geigy Co., describes in further detail this addition to the line of direct dyeing greens.

Patent Adjustment—Copyright Consolidation—Uniform State Regulations

By WALDON FAWCETT

The present autumn and winter will witness the development of three activities of significance to the cause of individuality or distinctiveness in industrial production and identification in commodity marketing. The first of this trio of hostages to progress is the adjustment of the U. S. Patent System to the advance of industry,—conspicuously the chemical industry. Second, comes the project for consolidation of the Federal machinery of copyright in order that it may function through a single agency. Third, is the campaign for the unanimous adoption of Uniform State laws covering trade marks, names, designs, devices and slogans.

ESSENTIALLY, the undertakings mentioned at the right are separate and distinct projects. At the same time, these several efforts for reform are interlocking and are interdependent in the sense that all share in the composite objective of more adequate protection for industrial property. All require, too, legislative action for their complete realization. In the case of two of the programs, Congressional approval is required. And it is because the appropriate committees of the national legislature have indicated a certain sympathy for the proposals that attention is warranted at this time. The third venture will be successful in proportion to its acceptance by the various State legislatures throughout the Union.

Patent Modernization

Broadly speaking, revision of the U. S. patent statutes is comparable to revision of the tariff, as a perennial issue. Scarcely a session of Congress runs its course without a minor or major operation in patent tinkering. The impending revolution is, however, in a class by itself in the intimacy and the practical character of its contacts with the dyestuffs industry. For one thing, the very scope or breadth of the realignment would render the contemplated shake-up notable in the eyes of the technical men in industry. As a second summons for the focusing of attention, there is the circumstance that this promised overhauling of the U. S. patent system is pre-eminently for the purpose of accommodation to the altered conditions and needs of industry. The adjustment of the patent system will not be accomplished solely and directly by legislative action. A portion of the desired improvements must come via innovations in administrative policy at the U. S. Patent Office. But this latter is already in process, thanks to the constructive attitude of the Patent Committees of the U. S. Senate and House of Representatives.

One of the prime requisites for a reconciliation of the U. S. Patent system to the needs of modern industry is an improvement in the methods of classification of patents. The task of classification devolves upon the Classification Division, a group of technical men whose function is to go over all patents and subdivide them according to channels of invention. The Classification Division has been chronically short of funds to do a complete job. Hence the criticism that the United States patents are not properly classified whereas, when it comes to foreign patents, the classification is extremely poor. This is a serious handicap in a field such as textile chemistry where in order to determine whether a fresh creation is actually unique and unanticipated, it is essential to make a comprehensive survey of existing achievements in the art abroad as well as in the United States.

According to qualified opinion, one of the main causes for the delays so often complained of, in issuance of U. S. patents, is the so-called interference procedure in the U. S. Patent Office. Out of a total of, say, 70,000 or 80,000 patent applications filed in a normal year there are perhaps 3,500 to 4,000 inventions, the right to each of which is claimed by two or more individuals. An "interference" is declared; the opposing parties file affidavits; and finally there are hearings before the Examiner of Interferences. Even that may not settle the matter, since an appeal is allowed to the Board of Appeals. The routine is complicated, costly, and time-consuming. One school of reformers believes that the whole institution of patent interferences should be done away with at the Patent Office and rival claimants be required to compose their difference in the Federal courts.

From the standpoint of the textile chemists and associated interests easily the most serious defect in the present patent system and the shining mark for reformation in the condition which prolongs, in the Patent Office, the pendency of applications. The factors above mentioned enter into this but there are other elements even more heavily responsible. In purchasing formulae, designs, processes or mechanical inventions, manufacturers and producers would, naturally, very much prefer to acquire assigned patents. But if the new discovery or invention is offered for fabrication promptly upon disclosure it is a foregone conclusion that the inventor has not a patent on which to negotiate but only an application for a patent. Under the system, as ordinarily operative, a period upward of a year, perhaps several years, may be required

to obtain a patent. Meanwhile the forces in a competitive industry which do not dare to hold off for the formal grant lest rivals supersede them, must make their contracts with inventors on the basis of "patents pending."

Supposing that there are 100,000 or more applications backed up awaiting official action it might appear that all that is necessary is to persuade Congress to provide additional appropriations to so man the Patent Office that official action could be taken on every application within, say, two months at the outside. Unfortunately the solution is not so simple. Because, it is not so much a lack of man-power which slows down the patent machinery at Washington as the propensity of patent lawyers to keep cases pending when it is to their interest to do so. There are, today, hanging fire at the Patent Office thousands of applications which have been pending for five years, or more, and some applications which have been marking time for as long as ten years. In not a few instances applications are studiously kept pending for years on end to permit further development of the inventions. Then, again, clients who are not ready to go on the market with an invention, instruct their attorneys to prolong the routine because the term of the patent (17 years) does not begin until the patent is actually granted and it is desirable that the concession shall not go into effect until the owner of the invention is ready to take full advantage of his franchise.

There is as yet no agreement as to precisely what course shall be pursued to discourage and restrict wilful tardiness in clearing patents. A time limit on suspended animation seems to be the indicated remedy. A group of leading manufacturers will advocate to Congress that after three years every pending patent application shall be "thrown open to inspection." This strikes at the vital spot in the technique of postponement. Inasmuch as, so long as applications are kept secret, manufacturers operating or desirous of operating in the field where the hidden invention is concealed must either move in the dark with their own improvements or else consider their hands tied.

Another argument that is being advanced at Washington in behalf of opening patent applications to inspection after a reasonable time is the necessity of circumventing unscrupulous manipulation. The maneuver is best described by Mr. G. H. Willitts of General Motors Corporation which has suffered through this stratagem. Said he: "Some companies file large numbers of patent applications and keep them in the Patent Office as long as they can. Perhaps they are already established in their field, supplying, say, a particular kind of machinery. They are afraid a competitor may come along with something just as good. They watch the market. As a competitor comes out with a new machine they examine the machine very carefully; they look through all their pending applications, which may run into several thousand, and see if they can't find some similarity, no matter how far-fetched, but some similarity between the competitive machine and the matter on the pending application, then they will write claims into the pending application covering this competitor's machine and in a short time come out with a patent, make charges of infringement, and bring suit. We had one situation of that sort where we were all ready to go into production on an accessory. The man with the pool of patents hidden in the Office knew of our activities. In that venture the loss to us in tools and dies ran into several hundred thousand dollars and it was a total loss. That thing has happened to industry after industry."

As Chairman of the Patents Committee of the American Institute of Chemical Engineers, Mr. R. S. McBride has, in season and out, emphasized at Washington "the importance of speed from the standpoint of the engineer." Developing this theme he said: "The engineer may be an investigator, a consultant, or a full-time employee of a corporation. The engineer has just as vital a part in the development of patents as the patent attorney who must handle the case in the Patent Office.

"For a number of years chemical engineers have been urging that the classification service of the Patent Office be improved. A very large part of the difficulty experienced by engineers in patent matters comes about because we cannot get facts. We cannot know just what has been in the Patent Office and where it lies with reference to new inventions. We therefore may appear to be making inventions when we are not. Or, we may fail to realize that we have made an invention when it has actually been accomplished.

"As far as I have heard expressions of opinion among chemical engineers they would decidedly favor the enactment of some provision to reduce the maximum time during which a patent may be kept in the Patent Office. They know that if a patent does not get into the Patent Office, get out on an adjudicated basis, and get into industry promptly, it is likely to be useless. Industry is advancing so fast that the majority of inventions which are accomplished today are worth nothing after ten years; what we have in industry becomes obsolete too fast. I find among technical men no desire to extend a patent because it expires for lack of usefulness before it expires by limitation of law.

"In the chemical field, we have another consideration of intercommodity competition. At the present time there is hardly any chemical which could not be displaced by some other chemical, even though it may not be quite so good. We have an almost impossible situation for anyone who desires to secure a monopoly of a particular use of a substance. There are so many ways of doing things nowadays that great monopolies under single commodity patents have become practically impossible."

The chemical engineers, among their other objectives in patent administrative reform, seek the determination of the exact status of inventions made by employees of the Federal Government or other public agencies. The present law on the subject is declared to be ambiguous. The chemical engineers approve the former official prac-

tice of the National Bureau of Standards—practice founded on the principles that if a Governmental investigation resulted in a discovery, the public should benefit, since it was the public's money which made possible the invention.

Copyright Coordination

Centralization of the Federal machinery of copyright has been advocated ever since the agitation for better protection for original designs for textiles resulted in the proposal to inaugurate the institution that would be known as Design Copyright or Design Registration. If the Design Patent system was to be supplanted by a special species of copyright for designs it was obviously appropriate that this new arm of copyright service should be administered in the same quarter as the copyright system already in existence for the fine arts. There now impends a second proposal for copyright consolidation only slightly less significant for the textile community than the design angle.

Put forward at this stage, in order that it may have full consideration in industry before the next session of Congress, is a proposal to transfer from the U. S. Patent Office to the U. S. Copyright Office, the existing facilities for the copyright of labels and "prints." To the color industry this merger would be more beneficial than might appear at first glance. It would put an end to the mystification and confusion which has now and again been occasioned by the circumstance that color plates, which rank as examples of the fine arts, are now cleared at one Federal agency whereas color-cards, etc., relating to articles of manufacture are cleared at another bureau. Prints and labels would be copyrighted more promptly than at present and probably with somewhat less expense.

Unfounded gossip has represented the officials at the U. S. Patent Office as opposing the transfer from their jurisdiction of labels, "prints" relating to articles of manufacture, etc. Commissioner of Patents Thomas E. Robertson assures The Reporter that not only is he favorable to the plan but that the Secretary of Commerce likewise approves the idea of such a transfer. Adding: "It is in the interest of economy and efficiency to place all copyright matters in the same office."

Standardization of State Laws

October, 1932, brings an important milestone in the progress of the long campaign to bring about, throughout the nation, uniformity of State laws for the protection of industrial property. This is the date when the National Conference of Commissioners on Uniform State laws receives, from its drafting committee, the tentative model of a Uniform State Trade Mark Law. In earnest of the significance for the dyestuffs industries, be it quickly added that the scope of the law is not restricted as the term "Trade Mark" might indicate. Identifying devices, individualistic designs, etc., have the same standing as commodity brands.

The movement to encourage, under the most influential auspices, all-States standardization of a statute destined to safeguard the intangible assets, holds out diverse and always practical promises. The gain is obvious for the business house which is operating solely in intra-state commerce instead of an interstate commerce and thus must rely upon State law, being denied the benefits of special Federal statutes. But there is likewise compensation for the marketer whose national distribution renders him eligible for Federal registration or certification service. If all States adopt the model statute, it will fall out that the average owner of symbols, patterns, or other good will assets, will find himself able to obtain broader protection via multiple State enrollments than he can obtain under the existing Federal laws.

The movement for Uniform State Laws protective of industrial property is receiving the active support of the American Bar Association which has, through the medium of a special committee of the best-qualified members, prepared its own version of a model statute. The Bar Association is the more in earnest because of faith that uniformity of State laws would, to a considerable extent, free business executives from a form of exploitation to which they have, latterly, been exposed in increasing degree—viz, solicitation by unethical agencies which offer their services to effect registrations under the present diverse State laws. The Bar Association declares that for this species of representation at State capitals, business men have been charged fees out of all proportion to the services actually rendered.

NOPCO Sales Manager

Officials of the National Oil Products Company of Harrison, N. J., have announced the appointment of Mr. Edson K. Rice as sales manager of their textile oils department in the mid-Western territory, with offices in Chicago.

Mr. Rice has a wide acquaintance in the textile field, having previously been affiliated with the Atlas Refining Company and for the past nine years with the John Campbell & Co. of New York City.

New Permutit Booklet

"No Scale, No Sludge, No Mud—The application of Zeolite Water Softeners to the treatment of Boiler Feed Water." This is the title of a very complete, interesting 36 page booklet just published by The Permutit Company, 440 Fourth Avenue, New York. It is profusely illustrated with photographs and diagrams and contains tabulated data, conversion tables, factors, reactions, etc. Copies may be obtained free upon request to the above company.

New Facts Concerning the Action of Caustic Alkalies on Cotton

(Continued from page 580)

vessel); it is then washed with distilled water and its "Abkochzahl" number determined. For this the fabric is repeatedly extracted with boiling 3% caustic soda and the extracts titrated with N/10 potassium permanganate solution until the extracts reach a constant value. The "Abkochzahl" number is then calculated from the total reducing power (expressed in terms of c.c. of N/10 potassium permanganate) of 100 grams of the cellulose. The method has been used extensively over a number of years by Kauffmann (Textilber., 1930, *11*, 122) and in spite of a certain amount of criticism from various workers its value appears to be established. The greater the action of the alkali-treatment the more is the cotton attacked in the treatment with sulphuric acid, and the higher is the resulting "Abkochzahl" number.

Having a satisfactory method for determining the degree of mercerization of a cotton, Rhomberg has investigated the effect of mercerizing liquors on cotton under various conditions. Thus it was found that the addition of ethyl alcohol to a mercerizing lye containing 20 grams of caustic soda per 100 c.c. at —1° C. has a slight adverse effect. On the other hand, the presence of common salt or sodium carbonate (up to half the weight of NaOH) in a mercerizing liquor was found, contrary to the results of other investigators, to have practically no deleterious effect on the mercerization.

At —1° C. it was found that equimolecular quantities of sodium and potassium hydroxides have about the same mercerizing effect! This is shown in Fig. 5.

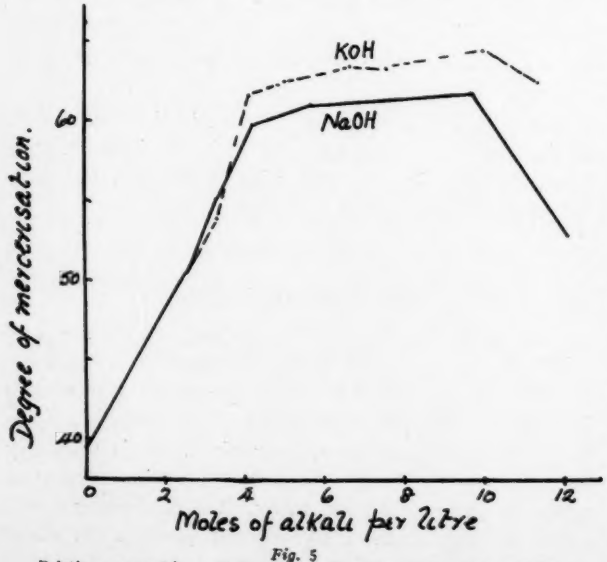

Fig. 5
Relative mercerizing effects of caustic soda and caustic potash.

Mercerization of cotton is a very rapid process and appears to be complete within ½ to 1 minute. A low temperature favors the process and —5° C. seems to be the optimum temperature. It is remarkable that at this temperature a liquor containing 10.4 grams of NaOH in 100 c.c. of water gives better mercerization than one containing 48.4 grams of NaOH. Apparently for each temperature of mercerization there is a particular concentration of caustic soda which gives the most satisfactory mercerization effect.

In the mercerization of cotton fabrics and yarns as usually carried out there is but little opportunity for absorption of oxygen from the air with consequent oxidation of the cotton to occur, but, as is well known, in the manufacture of viscose rayon sufficient time is allowed for such oxidation of the alkali-cellulose to take place; it is found that alkali-cellulose forms cellulose xanthogenate more readily if first slightly oxidized by exposure to the air. It would seem that there is a possibility of beneficially influencing the properties of mercerized cotton fabric by taking such steps that a controlled amount of oxidation can occur, and research along these lines appears definitely worth while. Those interested in this will find useful the recent publication by G. F. Davidson (J. Text. Inst., 1932, *23*, 95) which deals very fully with the aerial oxidation of cotton in contact with caustic alkalis.

Of course, the oxidation must not be allowed to proceed very far since then marked loss of strength would ensue. Thus the researches of Weltzien and Tobel (Ber. deut. chem. Ges., 1927, *60*, 2024 and Seide, 1927, *32*, 371 and 414) are not so valuable as they might have been since they deal with the destructive oxidation of cotton by aerial oxidation instead of simple modification. In the experiments of Davidson the degree of oxidation was limited to that produced by absorption of about 3.5 c.c. of oxygen per one gram of alkali-cellulose.

The oxidation of cotton in contact with caustic soda is found to depend on the concentration of alkali, the temperature of the reaction, the presence of impurities, and the pre-treatment of the cellulose.

The rate of oxidation of alkali-cellulose both at 40° C. and 60° C. increases rapidly when the concentration of sodium hydroxide is increased from 2.5 N. to 5 N. It then increases less rapidly as the concentration rises to about 10 N. where a well defined maximum rate of oxida-

TABLE I—OXIDATION OF ALKALI-CELLULOSE AT 40° C.

Concentration of NaOH. (Normality)	Volume of oxygen absorbed in c.c.	Duration of absorption in hours	Fluidity of resulting cellulose	Volume of oxygen absorbed per gram of cellulose at end of: 3 hrs.	6 hrs.	9 hrs.
2.50	0.34	25.5	13.3	0.02	0.05	0.09
5.00	1.32	10.8	30.9	0.24	0.64	1.07
7.37	2.28	10.0	39.7	0.44	1.16	2.01
10.33	2.93	10.2	45.9	0.58	1.46	2.51
12.72	2.63	10.0	45.4	45.4	1.37	2.32
15.20	2.21	10.0	41.8	0.50	1.20	1.95

tion becomes apparent; as the concentration of alkali is further increased the rate of oxidation falls. The effect of alkali concentration on oxidation is well shown in the curves of Figs. 6 and 7 and also in Table I.

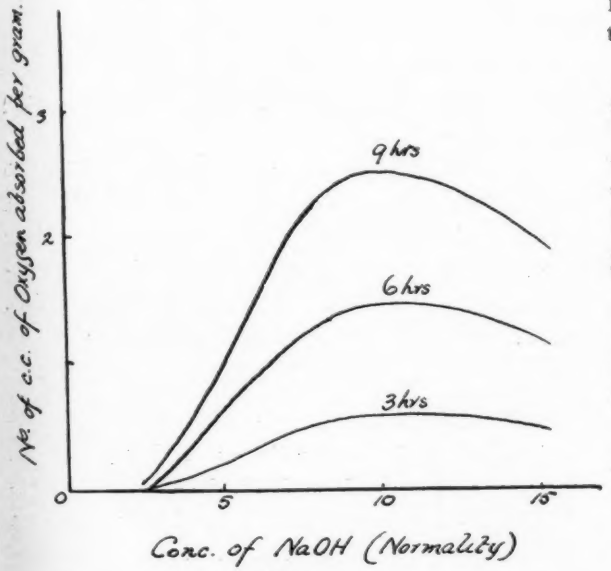

Fig. 6

Curves showing the number of c.c. of oxygen absorbed by alkali-cellulose at the end of 3, 6 and 9 hours while in contact with NaOH of increasing concentration.

It is also to be noticed that the degradation of the cellulose increases with the oxygen absorption and therefore this also has a maximum with caustic soda of about 10 N. The oxygen oxidation process becomes considerably more rapid when the temperature is maintained at 60° C. instead of 40° C. as shown in Table II below:

The above results were obtained when precautions were taken to remove all iron or other metallic impurities from the reaction mixture for it was found that iron by its catalytic influence much increased the rate of oxidation. Also other metals such as nickel, copper, and manganese had an accelerating influence on the course of the oxidation.

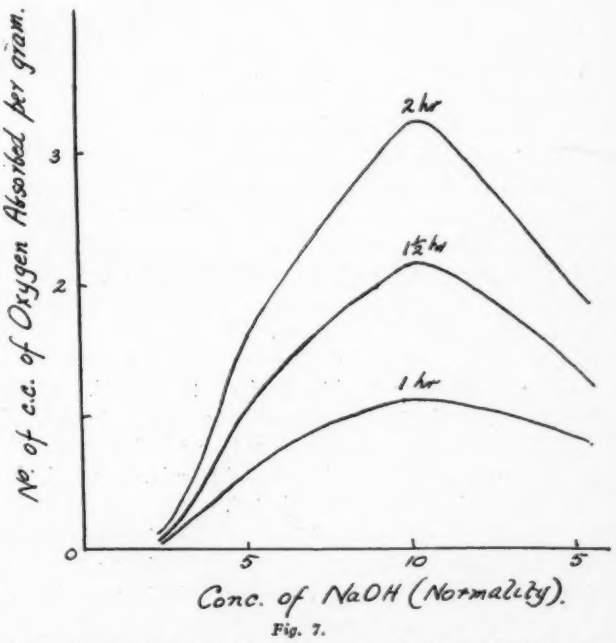

Fig. 7.

Curves showing the number of c.c. of oxygen absorbed by alkali-cellulose at the end of 1, 1½, and 2 hours while in contact with NaOH of increasing concentration.

It is generally known that cotton after treatment with an alkali has an increased reactivity and Davidson has now found that alkali treatment also increases the sus-

TABLE II—OXIDATION OF ALKALI-CELLULOSE AT 60° C.

Concentration of NaOH. (Normality)	Volume of oxygen absorbed in c.c.	Duration of absorption in hours	Fluidity of resulting cellulose	Volume of oxygen absorbed per gram of cellulose at end of: 3 hrs.	6 hrs.	9 hrs.
2.50	0.96	6.8	22.2	0.06	0.10	0.17
5.00	2.35	2.73	37.6	0.64	1.10	1.60
7.37	3.05	2.43	45.3	0.87	1.60	2.37
10.33	3.28	2.03	46.8	1.13	2.16	3.23
12.72	2.89	2.13	46.6	1.02	1.81	2.67
15.20	2.47	2.43	43.7	0.82	1.38	1.96

ceptibility of cotton to oxidation in air. The following results show this effect:

Concentration of NaOH used in pre-treatment with alkali. Normality	*Relative rate of oxidation in the presence of 2.5 N. NaOH*
0.00	1.00
5.00	2.09
7.37	2.20
10.33	2.42
12.72	2.56
15.20	2.51

Although it must be recognized that the oxidation of cotton in contact with alkali is much slower at 20° C. (ordinary room temperature) yet it does appear possible for a small degree of oxidation to occur in ordinary mercerizing processes. But if the alkali impregnated fabric is left lying about for some considerable time then there is a good possibility of oxidation occurring irregularly. This would lead to the formation of oxycellulose stains capable of resisting direct dyes. The presence of small amounts of iron in the mercerizing liquors would obviously assist such oxidation.

An interesting point in connection with these oxidation experiments is that the influence of the alkali concentration appears to be somewhat different from that observed in the acetylation experiments. It will be remembered that Scheidegger found the acetylation of cotton to be most influenced by a pre-treatment with caustic soda of at least 18.0% (about 4.5 N.). In the oxidation investigations it is found that the rate of oxidation increases with a pre-treatment with alkali up to 12.7 N. NaOH. Hence it must be inferred that the increase or decrease of reactivity of cellulose as produced by alkali treatment is intimately dependent on the type of reaction to which the alkali-treated cellulose is subjected.

The three papers to which reference is made above contain much information that cannot be dealt with here, but it is pointed out that they are worth the attention of all connected with the utilization of cellulosic fibers.

New Du Pont Dye

Ponsol Blue Green Y Double Paste, a vat dyestuff producing bright bluish greens said to be of very good fastness, especially to light, chlorine, washing and perspiration, has just been announced by the Dyestuffs Division of the du Pont Company.

In addition to possessing all the usual characteristics found in vat colors, it is said to give full shades dyed either cold or at higher temperatures. It is also stated that Ponsol Blue Green Y Double Paste is level dyeing, penetrates well, and is practically unaffected by metals.

The rate for "Position Wanted" advertisements in this column is 2 cents a word—with a minimum of 50 cents per insertion. For all other types of advertisements—i.e., help wanted, machinery or supplies for sale—the rate is $5.00 per column inch or less per insertion.

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EXPERIENCED SALESMAN - DEMONSTRATOR, Chicago Territory. Has thorough knowledge of all dyestuffs, imported as well as domestic, their application, and the use of all finishing materials, water softeners, penetrators, etc. Practical Dyehouse experience. References. Address Box No. 740, American Dyestuff Reporter, 440 Fourth Avenue, New York.

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WANTED by a large dyestuff manufacturer: Man to call on paint, varnish, lacquer, printing ink and color makers in the middle west. Selling experience preferable, although not absolutely essential. Write giving full particulars, etc. Box 749, care American Dyestuff Reporter.

SALESMAN—Wanted by a well established house, manufacturers of dyestuffs and chemicals. Young man about 35 years of age who has had experience in the selling of dyestuffs, sulphonated oils, finishes and softeners, in the Chicago and Middle west territory. State experience, technical training if any, salary, etc. Good opportunity for the right party. All replies will be treated strictly confidential. Address Box No. 750, American Dyestuff Reporter, 440 Fourth Avenue, New York.